PROBING MARTIAN SURFACE CHEMISTRY WITH LIBS: MAJOR AND MINOR ELEMENT ANALYSES WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY.

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Introduction: LIBS (Laser-Induced Breakdown Spectroscopy) will be used by ChemCam on the Mars Science Laboratory rover for remote elemental identification and quantification in rock and soil samples. LIBS uses a laser pulse focused onto a sample, creating a plasma of excited atoms and ions whose emissions give rise to spectroscopic features characteristic of specific ions and molecules.

Previous work on geological samples [1,2] has focused on quantification of major elemental abundances, e.g. Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti. These elements (with oxygen) typically account for >99% of the mass of the sample. We are currently expanding upon these studies by pursuing quantitative analysis of both minor elements, whose abundances are typically less than a few hundred parts per million [3], and other elements less routinely analyzed in terrestrial rocks such as H, C, S, and O. These elements are important for understanding Martian geochemistry.

However, quantitative elemental analyses using LIBS are possible only when chemical matrix effects, which influence the ratio of a given emission line to the abundance of the element producing that line, are considered. We present here a progress report from a multi-faceted study of methods for multi-element analysis of igneous rock types using LIBS.

Experimental: Samples for this study are the same as those used in [2], plus an additional 100 igneous samples with wide-ranging compositions. All samples were analyzed for major and minor elements in Michael Rhodes' XRF lab at the Univ. of Massachusetts using standard operating procedures [4] for internally-consistent results. H, S, and C were analyzed in the lab of Zach Sharp at UNM, where wt% H_2O is measured by reducing the samples at high temperatures with graphite, and the other elements are measured using an elemental analyzer.

The LIBS experimental conditions are chosen to mimic ChemCam operating conditions as closely as possible. Samples were placed in a vacuum chamber filled with 7 Torr CO_2. An Nd:YAG laser pulsing at 10 Hz produces the LIBS plasma. Spectra were obtained using three Ocean Optics HR2000 spectrometers covering the spectral ranges 223-326 nm (UV), 382-471 nm (VIS), and 495-927 nm (VNIR).

Results: We are exploring factors that affect the success of univariate and multivariate calibration techniques. For both methods, it is apparent that use of background-subtracted spectra for statistical analyses will produce superior quantatitive results. We are also currently comparing results of analyses using two different types of input: channel intensities vs. peak areas.

Multivariate methods are complicated by elemental correlations, both positive and negative, that arise from fundamental elemental substitutions. Because of this, it is important to make sure that predicted elemental abundances are substantially based on the emission lines of the element of interest and not simply on geochemically-related elements [3].

Partial Least Squares (PLS) methods for interpretation of LIBS spectra show great improvement over univariate methods [2]. Careful selection of samples used to build PLS models and attention to the compositional ranges they represent are critical to successful prediction of elemental abundances in unknown samples. PLS-2 results also highlight the influence that disparate concentration ranges can have on a regression model, and suggest that a key to obtaining good analyses for minor elements is normalization/rescaling of concentrations before input into statistical models.

PLS is only one of many multivariate regression techniques that could be used for calibration. Other techniques that explicitly take the issue of multicollinearity into account are also currently under investigation, such as forward and stepwise regressions. It is now clear that the LIBS technique has the capability to produce robust, quantitative analyses *not only* for major elements, but also for a large range of light elements and trace elements that are of great interest to geochemists. This list includes at least H, B, C, N, O, Be, Li, V, Cr, Ni, Sr, Zr, and Ba (in addition to major elements). ChemCam results from MSL should thus complement and expand upon those from the MERs and the Phoenix lander.

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